METHOD AND A DEVICE FOR PRODUCING AN ADHESIVE SURFACE ON A SUBSTRATE

CROSS-REFERENCE TO RELATED APPLICATION

This application claims the benefit of provisional application serial no. 60/465,923 filed April 24, 2003.

BACKGROUND ART

The present invention relates to a method and a device for producing an adhesive surface on a substrate, especially a silicon wafer. In general, the technique includes treating the surface to remove an oxide layer by wet chemical etching which results in a hydrophobic surface, and exposing the surface to a gaseous ozone atmosphere to provide a dry hydrophilic surface. The device includes a bath with an etchant for removing an oxide layer from the surface and a container having an inner volume that surrounds the bath, the inner volume also including a gaseous ozone atmosphere to produce a dry hydrophilic surface.

In 1986, Lasky and Shimbo succeeded in bonding two silicon wafers and in increasing the bonding strength by annealing so that further processing of a bonded wafer pair was possible. Currently, silicon wafer bonding is an important technology step in various parts of semiconductor technology such as in MEMS (Micro Electro Mechanical Systems) or in SOI technologies.

Hydrophobic and hydrophilic direct wafer bonding have to be differentiated depending on the specification of the silicon surface. A conventional silicon wafer normally has a native silicon dioxide layer on its surface that is a few Angströms thick. On this oxide layer, silanol sites (-Si-OH) are chemisorbed which absorb water molecules from the atmosphere so that a water film a few mono-layers thick is formed on the surface. This surface is water-attractive or hydrophilic. Hydrophilic surfaces are very reactive and therefore easily contaminated. When the hydrophilic silicon surface is exposed to a hydrofluoric acid solution, the silicon dioxide will be fully removed from the surface. The remaining pure silicon surface is saturated with hydrogen. Such a surface is water-repellent or hydrophobic.

In hydrophilic wafer bonding, hydrogen bonds, which are already formed at room temperature between the adjacent water molecules or the silanol sites of the opposite wafer surfaces, determine the bonding strength. A temperature treatment of the bonded wafers is used to change the chemical and physical structure of the bonding in the wafer. Between room temperature and about 200°C, the diffuse water molecules along the interface and closest Si-OH sites interact forming siloxane compounds (-Si-O-Si-). Between about 200°C and 900°C,

depending on the roughness of the bonded wafers, the water molecules can further diffuse to the pure silicon and react with the silicon by forming molecular hydrogen and silicon dioxide. Due to the migration of the interface water molecules, the silanol sites get closer to each other until they react or condense by forming a covalent siloxane compound splitting off a water molecule. A further annealing step at a temperature between about 800°C and 1000°C increases the bonding strength.

The wafers must be cleaned before bonding to remove organic and inorganic contaminants on the wafers. This can be achieved by a wet chemical cleaning and etching in one or more baths with cleaning fluids such as in a RCA-cleaning procedure or by dry chemical etching of contaminants, e.g. in an O_2-plasma.

Conventional RCA-cleaning is often complemented or replaced by other more effective cleaning methods. For example, the above-mentioned method could be used, as described in EP 0 731 495 B1, in which silicon wafers are cleaned in an etchant consisting of an aqueous solution containing hydrofluoric acid (HF) and a tenside, and wherein an ozone (O_3) gas flow flows through the solution. This etchant is especially suited for the removal of metallic or organic contamination on a silicon wafer. The increased solubility of ozone in aqueous HF leads to an increased formation of OH-radicals resulting in an enhanced particle reduction on the cleaned surfaces. In this method, after oxide removal, the HF concentration of the solution is reduced to 0% so that the ozone flows through pure DI-water, and the silicon wafer surfaces which were hydrophobic due to the HF treatment become hydrophilic after removal from the bath.

It is also necessary to provide an optimum amount of water on the wafer surface when using hydrophilic bonding methods. Too much water can lead to extensive water inclusions or water vapor bubbles at the bonding interface causing the wafers to de-bond. Therefore, a very accurate DI-water rinsing and drying method must be used with the wafers to apply only several mono layers of water on the wafer surfaces before bonding.

SUMMARY OF THE INVENTION

A method and device are presented for producing an adhesive surface on a substrate which can be bonded to another substrate. The method includes treating the surface by wet chemical etching to remove an oxide layer from the surface to provide a hydrophobic surface, and exposing the etched surface to a gaseous ozone atmosphere to provide a dry hydrophilic surface

The method may include one or more of the following features. The technique may further include utilizing an aqueous hydrofluoric acid solution (HF) as an etchant, or may include

utilizing an etchant that includes hydrofluoric acid (HF), ammonium fluoride (NH_4F) and water. The duration of wet chemical etching may be in the range of about 5 seconds to about 30 minutes, and the temperature of wet chemical etching may be in the range of between about room temperature to about 80°C. The method may include etching the substrate in a bath and taking the substrate out of the bath to directly contact a gaseous ozone atmosphere in a container volume.

A device for producing an adhesive surface on a substrate which can be bonded to another substrate is also provided. In an implementation, the device includes a bath with an etchant for removing an oxide layer from the surface of the substrate and to produce a hydrophobic surface, and a container having an inner volume that surrounds the bath. The inner volume also includes a gaseous ozone atmosphere to produce a dry hydrophilic surface.

A device according to the invention may include one or more of the following features. The device may include a sealed container, and may include an ozone generator coupled to the sealed container. The device may include at least one of a wafer holder, a sensor associated with the bath, a heating element coupled to the bath, and an outlet coupled to the container.

The present invention thus provides a method that is easy to carry out and a device that is suitable for effectively producing a bondable surface of the substrate. The method of the present invention is a very simple and efficient technique for producing an adhesive surface suitable for bonding. The surface sites of a pure surface, produced by wet chemical etching to remove an oxide layer on the surface, are simply saturated with oxygen in a gaseous atmosphere. Therefore, a pure oxide layer can be created on the surface of the substrate making the surface hydrophilic in a dry manner. This leads to an adhesive surface having an enhanced adhesion capability for bonding to another surface.

Use of the method according to the invention provides a substrate surface that is hydrophilic and dry. Moreover, use of the technique minimizes the chance of recontamination of the surface and results in an adhesive surface having a reduced particle concentration in comparison to a hydrophilic wafer surface produced in a wet manner.

According to the invention, the surfaces of silicon wafers are wet chemically etched only to remove silicon dioxide on the surface and results in a hydrophobic surface which can subsequently be made hydrophilic in the gaseous ozone atmosphere after chemical etching. A high density of silanol sites (Si-OH) are formed on the surface whereas only a small quantity of water molecules is absorbed on these sites.

Hydrofluoric acid is a good etchant of oxide, especially of silicon dioxide, which effectively removes the oxide on the surface of the substrate. The etchant may also include a

hydrofluoric acid, ammonium fluoride and water solution, which removes an oxide, especially silicon dioxide, on a surface like silicon with a high efficiency.

In the relatively short time of the duration of wet chemical etching of about 5 seconds to about 30 minutes, a native oxide on the surface of the substrate can be fully removed to get a pure surface of the substrate to form a good basis for the subsequent exposure to gaseous ozone. Similarly, use of an etch temperature for chemical etching in the range between room temperature of about 19°C to 25 °C and about 80°C, results in the effective removal of an oxide on the surface of the substrate to obtain a good basis for the subsequent exposure to a gaseous ozone atmosphere.

In the variant of the invention wherein the substrate is etched in a bath and then removed to contact the gaseous ozone, recontamination of the etched surface can be prevented because the etched surface can be immediately saturated with oxygen after being brought out of the etch bath.

The simple and efficient device according to the invention permits the substrate to be removed from the bath into a gaseous atmosphere. The surface of the substrate can then be effectively cleaned in the bath to result in a pure surface, and next the surface sites can be saturated in the gaseous ozone atmosphere with oxygen immediately after etching. The surface produced by this device has a good adhesion characteristic and is suitable for bonding.

Using a sealed container ensures that the required ozone concentration is reached and prevents any contamination from the outside. Therefore, it is possible to produce a uniform oxygen saturated surface with good hydrophilic properties. Use of an ozone generator coupled to the sealed container provides an ozone atmosphere in the equipment having a concentration which is high enough to saturate the surface sites on the etched surface with oxygen to get a well dried and hydrophilic substrate surface.

BRIEF DESCRIPTION OF THE DRAWINGS

Advantageous embodiments of the invention are described in the following description with reference to the accompanying figures, wherein:

Fig. 1 is a simplified diagram showing an embodiment of a device according to the present invention;

Figs. 2 to 7 show a silicon wafer, not drawn to scale, being processed according to an embodiment of the technique of the present invention, wherein:

Fig. 2 shows a silicon wafer with a native oxide on its surfaces before wet chemical etching;

Fig. 3 shows the silicon wafer of Fig. 2 during etching in a bath with an etchant;

Fig. 4 shows the silicon wafer of Figs. 2 and 3 after etching in the bath;

Fig. 5 shows the silicon wafer of Figs. 2 to 4 after removal from the bath and placement into an ozone atmosphere;

Fig. 6 shows the silicon wafer of Figs. 2 to 5 bonded with another silicon wafer directly after bonding; and

Fig. 7 shows the bonded wafer pair of Fig. 6 after a temperature treatment.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Fig. 1 shows a device 1 according to the present invention comprising a sealed container 2 with an inlet 3 coupled with an ozone generator 11 and with an outlet 4 coupled to a waste disposal device (not shown). A bath 5 is placed in the container 2. The bath 5 contains an etchant 6 consisting of an aqueous hydrofluoric acid solution (HF). The bath 5 can further comprise ozone. In an alternative embodiment, the bath can further contain ammonium fluoride (NH_4F). The bath is coupled with a heating element 10 by the which the temperature of the bath can be adjusted between room temperature which is approximately 19°C to 25°C, and about 80°C. The temperature is controlled with a sensor 13 in the bath. The bath can be recirculated and filtered to provide a homogenous temperature and concentration of the etchant 6 in the bath 5.

A wafer holder 8 is provided in the sealed container 2. The wafer holder 8 consists of an etch resistant material such as teflon. One or more silicon wafers 7 stand erect or inclined in the wafer holder 8. The wafers 7 are held on their edges by the wafer holder 8, so that their large flat surfaces are open and accessible to the fluid.

The inner volume 9 of the container 2 contains a gaseous ozone atmosphere 16 with an ozone concentration in a range between 1 to 15 parts per million (ppm). The atmosphere of the inner volume 9 can further contain HF vapour and air.

Figs. 2 to 7 show a silicon wafer 7 in different states according to an embodiment of the present invention.

Fig. 2 is a simplified side view of a silicon wafer 7 with native silicon oxide layers 12 on its large flat surfaces 15. The native oxide 12 may be a few Angström thick, respectively. As shown in Fig. 1, one or more wafers 7 in this state can be put into the wafer holder 8 to stand erect or inclined. Arrow A in Fig. 1 indicates that the wafer holder 8 including the wafer 7 is immersed in the bath 5 containing the etchant 6. Fig. 3 shows an immersed wafer wherein the etchant 6 fully surrounds the wafer 7. In this embodiment, the etchant 6 has a temperature of about 60°C. In another embodiment, the temperature of the etchant can be adjusted to another value between approximately room temperature and about 80°C.

As shown in Fig. 3, the etchant 6, especially the hydrofluoric acid solution (HF), reacts with the silicon dioxide 12. After several seconds to several minutes the native oxide 12 is fully removed from the surface 15. Fig. 4 shows that, after the native oxide is removed, the remaining pure silicon surface 15 is then essentially saturated with hydrogen (H).

Next, as shown in Fig. 5, the etched wafer 7 standing in the wafer holder 8 is taken out of the bath 5. Referring to Figs. 1 and 5, arrow B indicates that the wafer holder 8 including the wafer is brought directly into contact with the gaseous ozone atmosphere 16 surrounding the bath 5 in the inner volume 9 of the container 2. There, the ozone (O_3) reacts with the hydrogen on the wafer surface 15 to form silanol sites (-Si-OH) on the surface 15.

Fig. 6 shows two silicon wafers 7 which are etched as described, brought together by bonding equipment (not shown). The wafers are bonded in a conventional way laying one wafer 7 on the other wafer 7 and applying pressure on the upper wafer resulting in a spontaneous spreading of a bonding wave therebetween to form a bonded wafer pair. As shown in Figs. 6 and 7, the adjacent silanol sites (-Si-OH) of the opposite surfaces 15 of the wafers 7 react with each other at a certain temperature to form siloxane sites (-Si-O-Si-) and water. The wafers are then annealed at a temperature of about 500°C. The bonded wafers show a very good bonding strength in the range between 0.28 and 0.38 MPa at room temperature.

The described embodiment shows the method of the present invention with reference to silicon wafers, but the method can also be applied to any polished surfaces of metals, semiconductors and non-conductive materials which are bondable. The method can also be applied on only one silicon wafer which can be bonded with another silicon wafer having silicon dioxide on its surface. Furthermore, the wafer can be cleaned before wet chemical etching with conventional RCA-cleaning or plasma treating to obtain a pre-cleaned surface.